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(11) EP 0 695 765 A1

(12)

EUROPÄISCHE PATENTANMELDUNG

(43) Veröffentlichungstag:
07.02.1996 Patentblatt 1996/06

(51) Int. Cl.⁶: C08F 10/00

(21) Anmeldenummer: 95111478.4

(22) Anmeldetag: 21.07.1995

(84) Benannte Vertragsstaaten:
AT BE DE ES FR GB IT NL

(30) Priorität: 01.08.1994 AT 1512/94

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(54) Katalysatorsystem und Verfahren zur Polymerisation von Olefinen

(57) Katalysatorsystem auf Basis von Metallocenen, Aluminoxanen, organischen Übergangsmetallverbindungen und eines Katalysatorträgers. Die neuen Katalysatoren können vorteilhaft zur Polymerisation von Olefinen eingesetzt werden.

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Beschreibung

Die Erfindung betrifft ein heterogenes Katalysatorsystem für die Polymerisation von Olefinen, sowie ein Polymerisationsverfahren zur Herstellung von Polyolefinen, insbesondere von Polypropylenen (PP) bzw. dessen Copolymeren, die direkt im Reaktor als Blends von isotaktischen Polypropylenen und Stereoblock-Polypropylenen bzw. dessen Copolymeren erhalten werden.

Die Herstellung von Stereoblock-Polypropylenen bzw. elastomeren Polypropylenen (ELPP), die im wesentlichen eine stereoreguläre Blockanordnung im Kettenaufbau mit abwechselnden isotaktischen und ataktischen PP-Sequenzen in der Polymerkette besitzen, durch Polymerisation von Propylen, gegebenenfalls gemeinsam mit anderen Comonomeren, ist mit Hilfe spezieller Katalysatoren möglich. Solche Katalysatoren können beispielsweise metallorganische Ti-, Zr- oder Hf-Verbindungen auf einem Oxidträger (US 4335225), Metallocenkatalysatoren in Kombination mit Aluminoxanen (US 4522982) oder Reaktionsprodukte von Magnesiumalkoxiden mit einem tetravalenten Titanchlorid in Gegenwart spezieller Elektronendonatoren (US 5118 768) sein.

Bei der Aufarbeitung der mit diesen Katalysatoren hergestellten elastomeren Polypropylene zeigt sich jedoch, daß die Produkte sehr leicht agglomerieren und nicht frei fließend sind. Eine weitere Verarbeitung wird durch die Bildung von Klumpen sowie die Anhaftung und Verkebung an Transport- und Apparate teilen erschwert.

In DE-OS 43 21 496 wird dieser Nachteil beseitigt, indem ein spezieller Zr-Träger-Katalysator in flüssigem Propen verwendet wird und im Anschluß an die Polymerisation mit einem polaren Lösungsmittel oder mit CO₂ versetzt wird, um das gebildete Polypropylen auszufällen.

Desweiteren ist bekannt, daß man mit Metallocenen in Kombination mit Methylaluminoxanen isotaktisches Polypropylen (IPP) herstellen kann (Hoe EP-A-485823). Diese isotaktischen Polypropylene zeichnen sich durch ihre enge Molmassenverteilung und ihre hohe Kristallinität aus. Nachteil ist, daß die Produkte pulverförmig und damit für technische Anwendungszwecke untauglich sind.

Ebenso bekannt ist, daß Mischkatalysatoren bestehend aus einem Metallocen und einem konventionellen Ziegler-Natta-Katalysator, für die Herstellung von isotaktischen Polyolefinen, speziell von isotaktischem Polypropylen eingesetzt werden. Hierzu ist es erforderlich, das Metallocen auf dem heterogenen Ziegler-Natta-System zu fixieren. Die Polymerisate weisen einen hohen isotaktischen Anteil und eine breite Molmassenverteilung auf (Fina EP-A-0536104). Jedoch besitzen die Produkte eine hohe Steifigkeit, die für spezielle Anwendungen von Nachteil ist.

Durch Mischen von hochmolekularem, elastomerem PP und konventionellem isotaktischem PP kann man die beschriebenen Nachteile beseitigen und maßgeschneiderte, für den jeweiligen Einsatzzweck optimal geeignete Polymer-Blends herstellen. In DE-OS 43 30 341 werden ELPP/IPP-Blends als Knetermischungen beschrieben. Diese Blends zeichnen sich durch ihre erhöhte Rohfestigkeit bei herabgesetzter Steifigkeit aus, was für viele Anwendungen, wie z. B. bei der Herstellung von Folien, Schläuchen, Faltenbälgen etc. von Vorteil ist. Um diese hochmolekularen Mischungen technisch verarbeiten zu können, ist es erforderlich, beide Komponenten zusätzlich zum Mischvorgang zunächst in einem weiteren Verarbeitungsschritt im Extruder chemisch zu degradieren.

Es bestand somit die Aufgabe, ein Katalysatorsystem und ein Polymerisationsverfahren zu entwickeln, bei dem die beschriebenen Nachteile vermieden werden, und die es insbesondere ermöglichen, in einem einfachen Verfahren und direkt im Reaktor in einer "in situ"-Reaktion rieselfähige Polypropylen-Reaktorblends herzustellen.

Gelöst wurde die Aufgabe durch die Verwendung eines Katalysatorsystems auf Basis eines Metallocens, eines Aluminoxans, einer organischen Übergangsmetalverbindung und eines Katalysatorträgers.

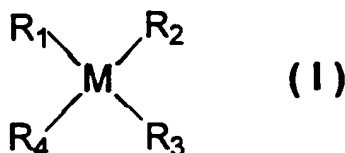
Gegenstand der Erfindung ist somit ein Katalysatorsystem zur Olefinpolymerisation, enthaltend

a) Metallocene von Übergangsmetallen der III., IV., V. und VI. Nebengruppe des Periodensystems, wobei unter die III. Nebengruppe auch die inneren Übergangselemente der Lanthaniden fallen;

b) Aluminoxane,

c) Metalloxide der II., III. und IV. Hauptgruppe des Periodensystems,

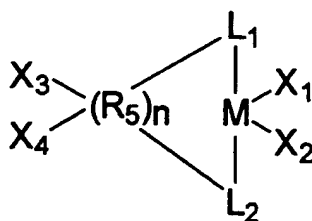
d) Organometallverbindungen der Formel I



worin

M ein Übergangsmetall der III., IV., V. oder VI. Nebengruppe des Periodensystems einschließlich der Lanthaniden und
 5 R₁ bis R₄ gleich oder verschieden sein können und einen Allyl-, Benzyl-, Neophyl- oder Neopentylrest bedeuten.

Als Metallocene können alle Verbindungen eingesetzt werden, die aus einem Übergangsmetall als Zentralatom und Koordinationsliganden auf Basis von substituierten oder unsubstituierten ein- oder mehrkernigen Kohlenwasserstoffen, die mit dem Zentralatom eine Sandwichstruktur bilden können, oder auf Basis von Amido-, Phosphido- oder Arsenido-
 10 resten aufgebaut sind, wobei die Koordinationsliganden auch über Brückenglieder verbunden sein können. Derartige Metallocene sind beispielsweise in DE-OS 44 17 542 (PCD), EP-A 336 128 (Hoechst) oder EP-A-536 104 (Fina) beschrieben. Bevorzugt werden Metallocene auf Basis von substituierten oder unsubstituierten, symmetrischen oder unsymmetrischen Cyclopentadienyl-, Indenyl- oder Fluorenyl-Metallocenen der Formel II,



(II)

worin M ein Übergangsmetall wie in Formel I darstellt,

30 X₁ bis X₄ gleich oder verschieden sind und eine C₁ - C₁₀-Alkylgruppe, eine C₁ - C₁₀- Alkoxygruppe, eine C₆ - C₁₀- Arylgruppe, eine C₆ - C₁₀- Aryloxygruppe, eine C₂ - C₁₀ -Alkenylgruppe, eine C₇ - C₂₀- Arylalkylgruppe, eine C₇ - C₂₀- Alkylarylgruppe, eine C₈ - C₂₀ - Arylalkenylgruppe, Wasserstoff oder ein Halogenatom bedeuten, L₁ und L₂ gleich oder verschieden sind und einen substituierten oder unsubstituierten Cyclopentadienyl-, Indenyl- oder Fluorenylrest darstellen,

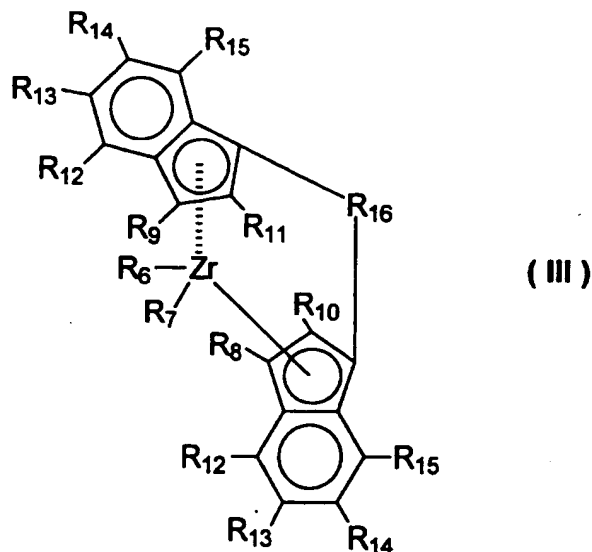
35 R₅ Kohlenstoff, Silizium, Germanium und Zinn sein kann,

n für eine ganze Zahl von 0 bis 4 steht, wobei für den Fall, daß n = 0 ist, die freien Valenzen an L₁ und L₂ durch einen Rest X₁ bis X₄ substituiert sind,

wie sie beispielsweise aus DE-OS 44 17 542 bekannt sind, eingesetzt.

Weiters bevorzugt sind Katalysatorsysteme, in denen das Zentralatom der Metallocene Ti, Zr oder Hf ist.

In Formel III ist beispielhaft ein weiteres erfindungsgemäß bevorzugt verwendbares Metallocen mit einem Zr-Zentralatom auf Basis von Indenyl-Koordinationsliganden gezeigt:



worin

R_6 und R_7

gleich oder verschieden sind und ein Halogenatom, eine C_1 - C_{10} -Alkylgruppe oder eine C_1 - C_{10} -Alkoxygruppe ist,

R_8 bis R_{11}

gleich oder verschieden sind und ein Wasserstoffatom, eine C_1 - C_{10} -Alkylgruppe oder eine C_6 - C_{10} -Arylgruppe ist,

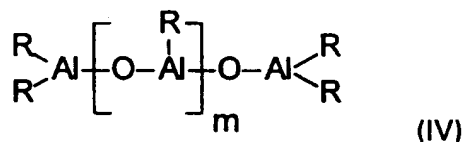
R_{12} bis R_{15}

gleich oder verschieden sind und ein Wasserstoffatom, eine C_1 - C_{10} -Alkylgruppe, eine C_6 - C_{10} -Arylgruppe, eine C_2 - C_{10} -Alkenylgruppe bedeuten und

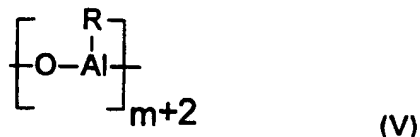
R_{16}

eine $-CH_2-CH_2-$, eine $Si(CH_3)_2$ oder eine $C(CH_3)_2$ -Brücke ist,

Als Aluminoxane können sowohl lineare



als auch cyclische Aluminoxane



eingesetzt werden, wobei in den Formeln IV und V die Reste gleich oder verschieden sein können und eine C_1 - C_6 -Alkylgruppe, eine C_6 - C_{10} -Aryl- bzw. Alkylarylgruppe bedeuten und m eine ganze Zahl von 1 - 50. Bevorzugt sind die Reste gleich und bedeuten Methyl, Isobutyl, Phenyl oder Benzyl, besonders bevorzugt ist Methyl. Das Aluminoxan kann

auf verschiedene Arten nach bekannten Verfahren hergestellt werden. Eine Möglichkeit ist beispielsweise die Umsetzung von Aluminiumalkylen mit kristallwasserhaltigem Aluminiumsulfat (Hoechst EP-A-302424). Besonders vorteilhaft wird handelsübliches MAO (Methylaluminoxan, Fa. Witco, BRD) verwendet.

Die anorganischen Oxide der Metalle der II. bis IV. Hauptgruppe des Periodensystems sind übliche Trägermaterialien für Katalysatoren. Bevorzugt sind die Oxide der Metalle Magnesium, Calcium, Aluminium, Silicium, Bor und deren Mischungen. Insbesondere bevorzugt sind z. B. die im Handel erhältlichen Aluminiumoxide "Alumina Typ C" (Fa. Degussa) und Siliciumoxide vom Typ "Silica Davison Grade 952 - 957", sowie Mischungen aus Al_2O_3 und SiO_2 . Vorteilhaft ist eine thermische Vorbehandlung des anorganischen Trägers im Inertgasstrom oder im Vakuum bei Temperaturen von 30 - 1000°C über einen Zeitraum von 1 - 50 Stunden. Diese thermische Vorbehandlung erfolgt vorzugsweise in einem Konditionierbehälter unter Vakuum bei Temperaturen von 200 - 800°C über einen Zeitraum von 2 - 8 Stunden.

Die Herstellung der Organometallverbindungen gemäß Formel I erfolgt beispielsweise analog den in US 3 932 307 und US 4 335 225 beschriebenen Verfahren. Eine Möglichkeit zu ihrer Herstellung ist die Umsetzung des Übergangsmetallhalogenids mit dem entsprechenden Grignard-Reagenz.

Die Herstellung des erfindungsgemäßen Katalysatorsystems erfolgt durch beliebiges Mischen der einzelnen Komponenten a) bis d). Es ist jedoch bevorzugt, daß zunächst die Metallocene (a) und Aluminoxane (b) miteinander vermischt werden, und diese Mischung sodann mit dem Reaktionsprodukt aus Metalloxiden (c) und Organometallverbindungen (d) vermischt wird. Es ist weiters bevorzugt, die einzelnen Komponenten in einem inerten Lösungsmittel, wie z. B. einem Kohlenwasserstoff zu mischen.

In einer weiters bevorzugten Art erfolgt die Herstellung des erfindungsgemäßen Katalysatorsystems in der Weise, daß zunächst die metallorganische Verbindung der Formel I mit dem thermisch behandelten Metalloxid umgesetzt wird. Die beiden Katalysatorkomponenten werden im allgemeinen im Verhältnis von etwa 0,01 bis 1 mmol der metallorganischen Verbindung pro Gramm Metalloxid umgesetzt. Bevorzugte Katalysatorkomponenten sind Tetraneophylzirkonium (TNZ) und hydroxyliertes Al_2O_3 . Die Herstellung dieses Katalysators wird beispielsweise in US 4335225 beschrieben.

In einem zweiten Schritt wird das Metallocen und das Aluminoxan auf den so vorbereiteten Katalysator aufgetragen. Dazu wird zunächst das Metallocen mit dem Aluminoxan gemischt. Das Mischen wird bevorzugt in Lösung vorgenommen, wobei das Metallocen beispielsweise in einem inerten Kohlenwasserstoff aufgelöst und mit einer Lösung des Aluminoxans vermischt wird. Als inerte Lösungsmittel eignen sich beispielsweise aliphatische oder aromatische Kohlenwasserstoffe, bevorzugt wird Toluol. Die Konzentration des Aluminoxans in der Lösung liegt im Bereich von etwa 5 bis 30 Gew.-% bezogen auf die Gesamtlösung. Die Metallocene werden vorzugsweise in einer Menge von 10^{-4} bis 1 mol pro mol Aluminoxan eingesetzt. Die Mischzeit beträgt 5 min bis 24 Stunden, vorzugsweise 5 bis 60 Minuten. Man arbeitet bei einer Temperatur von -10 bis +70°C, insbesondere bei 10 bis 40°C.

Die Auftragung der Metallocen/Aluminoxan-Reaktionsmischung auf den Trägerkatalysator (Metalloxid plus metallorganische Verbindung der Formel I) erfolgt bevorzugt in Lösung. Hierzu wird der Trägerkatalysator mit einem inerten Lösungsmittel unterschichtet und anschließend mit der Lösung des Metallocen/Aluminoxan-Komplexes verrührt. Als Lösungsmittel werden inerte aliphatische und aromatische Kohlenwasserstoffe bevorzugt. Insbesondere wird Toluol verwendet. Die Reaktionszeit beträgt 10 min bis 24 Stunden, vorzugsweise 10 bis 60 Minuten. Es wird bei einer Temperatur von 0 bis 80°C, insbesondere bei 10 bis 50°C gearbeitet.

Nach Beendigung der Reaktion wird das Lösungsmittel im Vakuum abgezogen, danach mit einem niedrigsiedenden, inerten Aliphaten mehrmals gewaschen. Bevorzugt wird n-Pentan eingesetzt. Der Metallocengehalt des dabei erhaltenen Katalysatorsystems liegt bevorzugt im Bereich zwischen 0,01 bis 1 Gew.-%, besonders bevorzugt zwischen 0,05 bis 0,3 Gew.-% bezogen auf die Masse des Gesamtkatalysators.

Das erfindungsgemäße Katalysatorsystem wird bevorzugt zur Polymerisation von Olefinen, wie z. B. Ethylen, Propen, Buten, 1-Buten, 1-Hexen, 4-Methyl-1-penten, 1-Octen, Cyclopenten, Norbornen oder Norbornadien eingesetzt.

Demnach ist ein weiterer Gegenstand der Erfindung die Verwendung des erfindungsgemäßen Katalysatorsystems zur Polymerisation von Olefinen.

Ein weiterer Gegenstand der Erfindung ist ein Verfahren zur Herstellung von Polyolefinen, bei dem die Olefine in Gegenwart des erfindungsgemäßen Katalysatorsystems polymerisiert werden. Besonders vorteilhaft ist die Herstellung von Polyolefin-Blends aus isotaktischen und elastomeren Polypropylenen, bei dem Propylen, gegebenenfalls gemeinsam mit weiteren Comonomeren, in Gegenwart des erfindungsgemäßen Katalysatorsystems polymerisiert wird.

Der besondere Vorteil der Verwendung des erfindungsgemäßen Katalysatorsystems liegt insbesondere darin, daß es möglich wird, direkt im Polymerisationsreaktor in einem Schritt "in situ" Polymer-Blends aus isotaktischen und elastomeren Stereoblock-Homo- und Copolymeren herzustellen, wobei sowohl der für derartige Blends bisher erforderliche Verfahrensschritt des Mischens, als auch die chemische Degradierung zur Erzielung von verarbeitungsfähigen Polymeren mit genügend niedriger Viskosität entfallen. Die erfindungsgemäß hergestellten Polymere sind gut rieselfähig, besitzen eine kompakte kugelförmige Gestalt und lassen sich gut verarbeiten.

Ein weiterer Vorteil liegt darin, daß es möglich ist, Polymer-Blends mit hohen Molmassen, sowie mit breiter und/oder bimodaler Molmassenverteilung herzustellen. So ist es beispielsweise möglich, in einem Schritt sowohl hochmolekulare elastomere PP, als auch niedermolekulare isotaktische PP direkt im Reaktor herzustellen.

Der erfindungsgemäße Katalysator kann sowohl als Pulver, als auch als Suspension in einem inerten Kohlenwasserstoff, beispielsweise Pentan, Hexan, Cyclohexan oder Mineralölen, in die Polymerisationsmischung eingebracht werden. Die Polymerisation wird in bekannter Weise in Lösungs-, Suspensions- oder Gasphasenverfahren, kontinuierlich oder diskontinuierlich bei einer Temperatur von -10 bis +200°C, vorzugsweise +20 bis +80°C durchgeführt. Polymerisiert wird Propen, gegebenenfalls gemeinsam mit weiteren Comonomeren wie z.B. Ethylen, 1-Buten, 1-Hexen, 4-Methyl-1-penten, 1-Octen, Cyclopenten, Norbornen oder Norbornadien. Als Molmassenregler wird, falls erforderlich, Wasserstoff zugegeben. Der Gesamtdruck der Polymerisation beträgt 0,5 - 150 bar. Bevorzugt ist die Polymerisation in dem Druckbereich von 1 bis 40 bar.

Die Menge der eingesetzten Trägers beträgt 0,1 bis 1g pro Liter Reaktorvolumen, insbesondere 0,2 bis 0,6g pro Liter Reaktorvolumen. Die Menge der Übergangsmetallverbindungen, bezogen auf das Übergangsmetall, beträgt 10^{-3} bis 10^{-8} mol Übergangsmetall, vorzugsweise 10^{-4} bis 10^{-7} mol pro Gramm Träger. Das Aluminoxan wird in einer Konzentration von 10^{-6} bis 10^{-1} mol, vorzugsweise 10^{-5} bis 10^{-2} mol pro Gramm Träger eingesetzt.

Wenn die Polymerisation als Suspension- oder Lösungspolymerisation durchgeführt wird, wird ein inertes Lösemittel verwendet. Beispielsweise können aliphatische oder cycloaliphatische Kohlenwasserstoffe, wie Pentan, Hexan oder Cyclohexan verwendet werden. Brauchbar ist auch Toluol. Bevorzugt wird im flüssigen Monomeren polymerisiert. Werden inerte Lösungsmittel eingesetzt, wird Propen gasförmig oder flüssig zudosiert.

Die Dauer der Polymerisation beträgt 10 min bis 6 Stunden, bevorzugt eine bis drei Stunden.

Die nachfolgenden Beispiele sollen die Erfindung näher erläutern.

Es bedeuten:

M_w gewichtsmittlere Molmasse in g/mol } ermittelt durch GPC
 M_w/M_n Molmassendispersität

MFI(230/2,16) Schmelzindex, gemessen nach DIN 53735; 230°C Schmelztemperatur und 2,16 kg Belastung

T_{m1} Schmelztemperatur 1 in °C }
 T_{m2} Schmelztemperatur 2 in °C } ermittelt durch DSC
 ΔH Schmelzenthalpie in Joule/g }

A) Herstellung des Katalysators

1) Herstellung des Tetraneophylzirconium (TNZ) /Al₂O₃-Trägerkatalysators

Unter Schutzgas wird 21,59 g gereinigtes TNZ (Herstellung gemäß DE-OS 43 21 496) in 300 ml trockenem Hexan gelöst und in einen Tropftrichter überführt, anschließend wird die so vorbereitete Lösung langsam unter Rühren einer Suspension aus 171,25g Al₂O₃ und 3,25 l Hexan zugetropft und 14h bei Raumtemperatur gerührt. Das verwendete Aluminiumoxid wird in einen ausgeheizten und mit Stickstoff gespülten Konditionierbehälter gefüllt und 4h unter Vakuum bei 385°C gegläht und entgast, anschließend unter Stickstoff-Überdruck abgekühlt und bei einem bar bis zum Einsatz gelagert. Nach Beendigung der Reaktion wird das überschüssige Lösungsmittel abgezogen und anschließend im Vakuum bis zur Gewichtskonstanz getrocknet. Der so erhaltene Trägerkatalysator weist einen TNZ-Gehalt von 11,89 Ma-% auf. Unter Stickstoff ist er beliebig lange haltbar.

2) Fixierung des Metallocen/MAO-Komplexes auf den TNZ/Al₂O₃-Trägerkatalysator

7,5 mg Ethylenbis(indenyl)zirkoniumdichlorid (Fa. Witco) wird unter Stickstoff in 10 ml Toluol gelöst. Anschließend wird 4,95 g einer 10,5 Masse-%-igen MAO-Lösung (Methylaluminoxan, Fa. Witco) langsam unter Rühren zugetropft und 15 min gerührt. Die so erhaltene Katalysatorlösung wird mit einer Spritze aufgenommen und unter Rühren zu 5,48g des unter 1) hergestellten TNZ/Al₂O₃-Trägerkatalysator zugesetzt. Danach wird 45 min bei Raumtemperatur nachgerührt, anschließend unter Vakuum das Lösungsmittel abgezogen, mit 20 ml Pentan zweimal gewaschen und getrocknet. Der so hergestellte Katalysator weist einen Metallocengehalt von 0,08 Masse-% auf. Das Molverhältnis Al(MAO) : Zr (MC) beträgt 500 : 1.

B) PolymerisationBeispiel 1

5 Ein bei 160°C und 0,1 mbar ausgeheizter 5 l - Doppelmantel-Autoklav mit Rührer, Thermostatmantel, Temperatur-, Drehzahl- und Drehmomentmessung wurde nach drei Propen/Vakuumzyklen mit 500 g Propen bei 16°C befüllt. Nach Erhöhung der Rührgeschwindigkeit auf 400 U/min und Aufheizung des Systems auf 30°C wurden 2g des unter A2) beschriebenen Katalysators mit 1000g Flüssigpropen eingespült. Innerhalb von 10 min wurde der Reaktor auf eine Arbeitstemperatur von 60°C aufgeheizt und dabei die Rührgeschwindigkeit auf 700 U/min erhöht. Nach einer Polymerisationszeit von 2h wurde die Rührerdrehzahl auf 150 U/min gesenkt und das überschüssige Propylen unter Beibehaltung der Arbeitstemperatur abgelasht, nochmals mit Stickstoff gespült, anschließend der Reaktor geöffnet. Das verbliebene Polymer war rieselfähig, nichtklebend und kugelförmig. Nach Stabilisierung und Trocknung im Vakuumschrank bei 50°C erhielt man 71 g Polymer (Analysendaten siehe Tabelle 1).

15 Beispiel 2

Beispiel 1 wurde wiederholt, der Katalysator wies jedoch einen Metallocenanteil von 0,125 Ma-% auf, das Molverhältnis Al(MAO) : Zr(Metallocen) betrug 250 : 1. Die Reaktionszeit betrug 2h, die Polymerisationstemperatur 60°C. Das verbleibende Polymerprodukt war kugelförmig, rieselfähig und nichtklebend. Es wurden 78 g erhalten (Vgl. Tab. 1).

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Beispiel 3

Die Polymerisation erfolgte analog Beispiel 1, jedoch wies der Katalysator ein Metallocengehalt von 0,125 Ma-% auf, das Al(MAO) : Zr(Metallocen)-Verhältnis betrug 125 : 1. Die Polymerisationstemperatur betrug 60°C, die Polymerisationsdauer 2h.

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Erhalten wurde ein elastisches Polymerprodukt von feinkörniger, rieselfähiger Struktur. Es wurde nach der Aufarbeitung entsprechend Beispiel 1 eine Ausbeute von 107 g erzielt.

Beispiel 4:

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2,08 g des unter A2) hergestellten Katalysators wurden analog Beispiel 1 zur Polymerisation von Propen eingesetzt. Jedoch wies der Katalysator einen Metallocengehalt von 0,288 Ma-% auf. Das Al(MAO) : Zr(Metallocen) - Verhältnis betrug 125 : 1. Die Polymerisationstemperatur betrug 60°C, die Polymerisationsdauer 2h. Das erhaltene Polymer war rieselfähig, nichtklebend und wies eine breite Korngrößenverteilung auf. Die Ausbeute des aufgearbeiteten Produktes betrug 201g (Vgl. Analysenergebnisse Tab. 1).

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Beispiel 5:

2,12g des unter A2) hergestellten Katalysators (Metallocengehalt 0,283 Ma-%) wurden gemäß Beispiel 1 zur Polymerisation von Propen eingesetzt. Das Al(MAO) : Zr(Metallocen)-Verhältnis betrug 125:1. Im Unterschied zu Beispiel 1 wurden 1300g Propen vorgelegt, der Katalysator bei der Polymerisationstemperatur von 60°C mit 200g Propen und einem Stickstoffdruck von 40bar eingespült. Die Reaktionsdauer betrug 2h. Nach Beendigung der Polymerisation erhielt man ein rieselfähiges, körniges Produkt. Die Ausbeute betrug 51g.

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45 Beispiel 6

Die Polymerisation erfolgte analog Beispiel 5. Die Katalysatormenge betrug 2g mit einem Metallocengehalt von 0,1 Ma-%. Das Al(MAO) : Zr(Metallocen)-Verhältnis betrug 250 : 1. Es konnte eine Ausbeute von 105,4 g erhalten werden. Das Produkt war rieselfähig und von körniger Struktur.

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Beispiel 7:

Beispiel 6 wurde wiederholt, der Metallocengehalt betrug 0,2 Ma-%. Nach 2 Stunden wurde die Polymerisation abgebrochen. Erhalten wurden 381,2 g eines rieselfähigen, kugelförmigen, nichtklebenden Produktes.

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Beispiel 8:

Die Polymerisation von Beispiel 6 wurde wiederholt, jedoch lag der Metallocengehalt des Katalysators bei 0,3 Ma-%. Es konnte eine Ausbeute von 652,3 g erzielt werden. Das Produkt war rieselfähig und feinkörnig.

Vergleichsbeispiel I:

2,03g eines reinen TNZ/ Al_2O_3 -Trägerkatalysators wurden mit MAO analog Beispiel A2) umgesetzt. Auf die Zugabe von Metallocen wurde verzichtet. Das Molverhältnis MAO : Zr(TNZ) betrug 5 : 1. Die Polymerisation erfolgte analog
5 Beispiel 1, wobei 17g eines zum Kleben neigenden, nicht rieselfähigen Polymerproduktes erhalten wurden. Das Polymer

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ist für eine Weiterverarbeitung ungeeignet.

Tabelle 1:

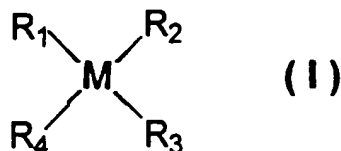
Beispiel	Aktivität (kg PP/mol Zr ⁴⁺ h)	M _w (g/mol)	M _w /M _n	MFI (g/10min)	T _{m1} (°C)	T _{m2} (°C)	Δ H 1 (J/g)	Δ H 2 (J/g)
1	83,7	979000	32	0,67	134	148	40	13
2	93,6	828000	25	1,23	133	148	41	13
3	126,1	2200000	6	<0,01	131	151	-	-
4	236,5	920000	27	172	132	151	-	-
5	251,2	854000	26	226	133	153	-	-
6	128,1	-	-	699	134	151	-	-
7	468	925000	15	<0,01	132	152	-	-
8	807,9	1990000	10	<0,01	131	152	-	-
Vergleichsbeispiel I	53,7	n.b.*	n.b.*	n.b.*	-	148	-	-

*n. b. nicht bestimmbar (Ausschlußgrenze GPC)

Patentansprüche

1. Katalysatorsystem zur Olefinpolymerisation, enthaltend

- 5 a) Metallocene von Übergangsmetallen der III., IV., V. und VI. Nebengruppe des Periodensystems,
 b) Aluminoxane,
 c) Metalloxide der II., III. und IV. Hauptgruppe des Periodensystems,
 d) Organometallverbindungen der Formel I



20 worin

M ein Übergangsmetall der III., IV., V. oder VI. Nebengruppe des Periodensystems und
 R1 bis R4 gleich oder verschieden sein können und einen Allyl-, Benzyl-, Neophyl- oder Neopentylrest bedeuten.

- 25 2. Katalysatorsystem gemäß Anspruch 1, dadurch gekennzeichnet, daß Metallocene auf Basis von substituierten oder unsubstituierten, symmetrischen oder unsymmetrischen Cyclopentadienyl-, Indenyl- oder Fluorenyl-Metallocenen vorliegen.
- 30 3. Katalysatorsystem gemäß Anspruch 1 oder 2, dadurch gekennzeichnet, daß Metallocene auf Basis von Ti, Zr, Hf vorliegen.
- 35 4. Verfahren zur Herstellung eines Katalysatorsystems gemäß einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß zunächst die Metallocene (a) und Aluminoxane (b) miteinander vermischt werden, und diese Mischung sodann mit dem Reaktionsprodukt aus Metalloxiden (c) und Organometallverbindungen (d) vermischt wird.
5. Verwendung des Katalysatorsystems gemäß einem der Ansprüche 1 bis 3 zur Polymerisation von Olefinen.
- 40 6. Verfahren zur Herstellung von Polyolefinen, dadurch gekennzeichnet, daß Olefine in Gegenwart des Katalysatorsystems gemäß einem der Ansprüche 1 bis 3 polymerisiert werden.
7. Verfahren zur Herstellung von Polyolefin-Blends aus isotaktischen und elastomeren Polypropylenen, dadurch gekennzeichnet, daß Propylen, gegebenenfalls gemeinsam mit weiteren Comonomeren, in Gegenwart des Katalysatorsystems gemäß einem der Ansprüche 1 bis 3 polymerisiert wird.



Europäisches
Patentamt

EUROPÄISCHER RECHERCHENBERICHT

Nummer der Anmeldung
EP 95 11 1478

EINSCHLÄGIGE DOKUMENTE			
Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich, der maßgeblichen Teile	Betrifft Anspruch	KLASSIFIKATION DER ANMELDUNG (Int.Cl.6)
X	WO-A-87 02991 (EXXON CHEMICAL PATENTS INC) * Ansprüche 1,7,9,12 * * Seite 7, Zeile 16 - Zeile 33 * ---	1-3,5,6	C08F10/00
A	EP-A-0 546 690 (NIPPON OIL CO LTD) * Seite 24; Beispiel IE29; Tabelle 3 * ---	1	
A	US-A-4 411 821 (EDWARD G. HOWARD) * Anspruch 1 * * Beispiele 1,2 * -----	1	
			RECHERCHIERTE SACHGEBIETE (Int.Cl.6)
			C08F
Der vorliegende Recherchenbericht wurde für alle Patentansprüche erstellt			
Rechercheamt DEN HAAG		Abschließdatum der Recherche 27.Oktober 1995	Prüfer Fischer, B
KATEGORIE DER GENANNTE DOKUMENTE X : von besonderer Bedeutung alleine betrachtet Y : von besonderer Bedeutung in Verbindung mit einer anderen Veröffentlichung derselben Kategorie A : technologischer Hintergrund O : mündliche Offenbarung P : Zwischenliteratur T : der Erfindung zugrunde liegende Theorien oder Grundsätze E : älteres Patentdokument, das jedoch erst am oder nach dem Anmeldedatum veröffentlicht worden ist D : in der Anmeldung angeführtes Dokument L : aus anderen Gründen angeführtes Dokument & : Mitglied der gleichen Patentfamilie, übereinstimmendes Dokument			

EPO FORM 1501 (6.12.92) (P04/00)

FTO 00-1653

European Patent No. EP 0 695 765 A1

A CATALYST SYSTEM AND METHOD FOR POLYMERIZATION OF
OLEFINS

Dr. Eberhard Ernst et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. MARCH 2000
TRANSLATED BY THE RALPH MCELROY TRANSLATION COMPANY

EUROPEAN PATENT OFFICE
EUROPEAN PATENT NO. EP 0 695 765 A1

Int. CL ⁶ :	C 08 F 10/00
Filing No.:	95111478.4
Filing Date:	July 21, 1995
Publication Date:	February 7, 1996 Patent Bulletin 1996/06
Priority:	
Date:	August 1, 1994
Country:	AT
No.:	1512/94
Designated Contracting States:	AT, BE, DE, ES, FR, GB, IT, NL

A CATALYST SYSTEM AND METHOD FOR POLYMERIZATION OF
OLEFINS

[Katalysatorsystem und Verfahren zur Polymerisation von Olefinen]

Applicant:	PCD-Polymere Gesellschaft m.b.H.
Inventors:	Dr. Eberhard Foust et al.

Description

The invention concerns a heterogeneous catalyst system for polymerization of olefins, and a polymerization method for production of polyolefins, especially propylenes (PPs) or their copolymers, which are obtained directly in the reactor as blends of isotactic polypropylenes and stereoblock polypropylenes or their copolymers.

The production of stereoblock polypropylenes or elastomeric polypropylenes (ELPPs), which on the whole have a stereoregular block arrangement in the chain structure with alternating isotactic and atactic PP sequences in the polymer chain, by polymerization of propylene, optionally together with other copolymers, is possible with the aid of particular catalysts. Such catalysts can, for example, be organometal Ti, Zr or Hf compounds on an oxide

support (US 4335225), metallocene catalysts in combination with aluminoxanes (US 4522982) or reaction products of magnesium alkoxides with tetravalent titanium chloride in the presence of particular electron donors (US 5118 768).

However, in the further processing of elastomeric polypropylenes made with these catalysts, it turns out that the products agglomerate very readily and are not free flowing. Further processing is impeded by the formation of clumps as well as by the adhesion and bonding to transport and equipment parts.

This disadvantage is remedied in DE-Patent Application [OS; Offenlegungsschrift] 43 21 496 by using a particular Zr support catalyst in liquid propene and at the end of polymerization adding a polar solvent or CO₂ in order to precipitate the polypropylene as formed.

In addition, it is known that isotactic polypropylenes (IPPs) can be produced with metallocenes in combination with methylaluminoxanes (Hoe [Hoechst] EP-A-485823). These isotactic polypropylenes are characterized by narrow molecular weight distribution and high crystallinity. A disadvantage is that the products are in powder form and thus are unserviceable for industrial applications.

It is also known that mixed catalysts consisting of a metallocene and a conventional Ziegler-Natta catalyst are used for the production of isotactic polyolefins, in particular isotactic polypropylene. For this it is necessary that the metallocene be immobilized on the heterogeneous Ziegler-Natta system. The polymerizates have a high isotactic proportion and broad molecular weight distribution (Fina EP-A-0536104). However, the products have high rigidity, which is disadvantageous for particular applications.

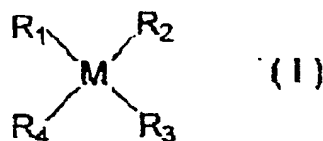
The described disadvantages can be remedied and tailored polymer blends that are optimally suitable for the relevant use can be produced by mixing high-molecular, elastomeric PP and conventional isotactic PP. ELPP/IPP blends are described as kneader mixtures in DE-OS 43 30 341. These blends are characterized by their elevated raw strength with reduced stiffness, which is advantageous for many applications such as, for example, in the production of films, tubes, corrugated expansion joints, etc. In order to be able to process these high-molecular mixtures industrially, it is necessary first to degrade the two components chemically in an extruder in an additional process step, in addition to the mixing operation.

Thus, there was the task of developing a catalyst system and a polymerization method in which the described disadvantages are avoided and which enables in particular free flowing polypropylene reactor blends to be produced in a simple method and directly in the reactor in an "in situ" reaction.

The task was solved through the use of a catalyst system based on a metallocene, an aluminoxane, an organic transition metal compound and a catalyst support.

The object of the invention is thus a catalyst system for olefin polymerization, which contains

- a) Metallocenes of transition metals of the III, IV, V and VI subgroups of the periodic system, where the inner transition elements of the lanthanides also fall under subgroup III,
- b) Aluminoxanes,
- c) Metal oxides of main groups II, III and IV of the periodic system,
- d) Organometal compounds of formula I

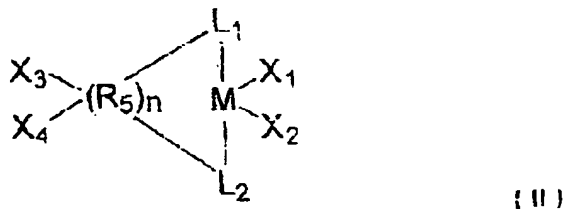


where

M is a transition metal of the subgroups III, IV, V or VI of the periodic system, including the lanthanides and

R_1 to R_4 can be the same or different and mean an allyl, benzyl, neophyl or neopentyl residue.

All compounds that are formed from a transition metal as central atom and coordination ligands based on substituted or unsubstituted mononuclear or polynuclear hydrocarbons that can form a sandwich structure with the central atom or are formed on the basis of amido, phosphido or arsenido residues, where the coordination ligands can also be bonded via bridge members can be used as metallocenes. Metallocenes of this kind are described, for example, in DE-OS 44 17 542 (PCD), EP-A 336 128 (Hoechst) or EP-A-536 104 (Fina). Metallocenes based on substituted or unsubstituted, symmetric or asymmetric cyclopentadienyl, indenyl or fluorenyl metallocenes of formula II are preferred,



where M represents a transition metal as in formula I,

X_1 to X_4 are the same or different and mean a C_1 - C_{10} alkyl group, a C_1 - C_{10} alkoxy group, a C_6 - C_{10} aryl group, a C_6 - C_{10} aryloxy group, a C_2 - C_{10} alkenyl group, a C_7 - C_{20} arylalkyl group, a C_7 - C_{20} alkylaryl group, a C_8 - C_{20} arylalkenyl group, hydrogen or a halogen atom,

L_1 and L_2 are the same or different and represent a substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl residue,

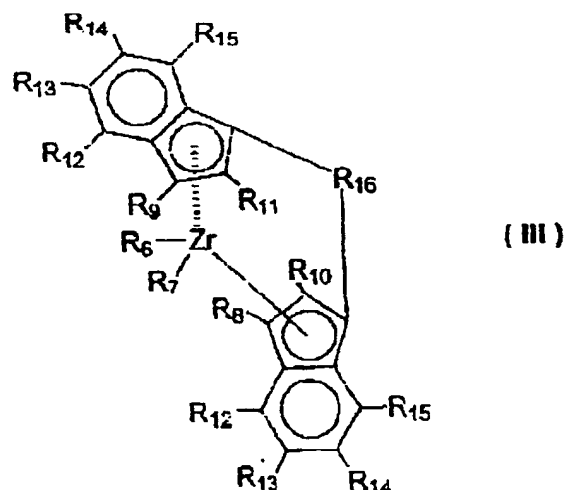
R_5 can be carbon, silicon, germanium and tin,

n stands for a whole number from 0 to 4, where for the case that $n = 0$, the free valences on L_1 and L_2 are substituted by a residue X_1 to X_4 .

such as are known, for example, from DE-OS 44 17 542.

Additionally preferred are catalyst systems in which the central atom of the metallocenes is Ti, Zr or Hf.

Formula III shows as an example another metallocene that can be preferably used in accordance with the invention, with a Zr central atom based on indenyl coordination ligands:



where

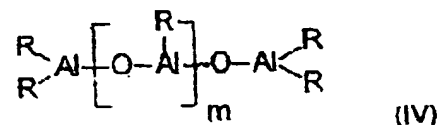
R_6 and R_7 are the same or different and represent a halogen atom, a C_1 - C_{10} alkyl group or a C_1 - C_{10} alkoxy group,

R_8 to R_{11} are the same or different and represent a hydrogen atom, a C_1 - C_{10} group or a C_6 - C_{10} aryl group,

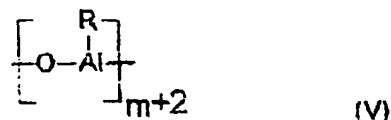
R_{12} to R_{15} are the same or different and mean a hydrogen atom, a C_1 - C_{10} alkyl group, a C_6 - C_{10} aryl group, a C_2 - C_{10} alkenyl group and

R_{16} is a $-\text{CH}_2-\text{CH}_2-$, an $\text{Si}(\text{CH}_3)_2$ or a $\text{C}(\text{CH}_3)_2$ bridge.

Both linear



and cyclic



aluminoxanes can be used as (aluminoxanes, where in formulas IV and V the residues can be the same or different and mean a C_1-C_6 alkyl group, a C_6-C_{10} aryl or alkylaryl group and m is a whole number from 1 to 50. Preferably the residues are the same and mean methyl, isobutyl, phenyl or benzyl, especially preferably methyl. The aluminoxane can be produced in various ways by known methods. One possibility, for example, is the reaction of aluminum alkyls with aluminum sulfate that contains water of crystallization (Hoechst EP-A-302424). Commercially available MAO (methylaluminoxane, Witco, FRG) is used with particular advantage.

The inorganic oxides of the metals of main groups II to IV of the periodic system are the usual support materials for catalysts. Preferred are the oxides of the metals magnesium, calcium, aluminum, silicon, boron and their mixtures. Especially preferred are, for example, the commercially available aluminioxides "Alumina type C" (Degussa) and silicon oxides of type "Silica Davison Grade 952-957," as well as mixtures of Al_2O_3 and SiO_2 . Thermal pretreatment of the inorganic support in an inert stream of gas or in a vacuum at temperatures of $30-1000^\circ\text{C}$ for periods of 1-50 h is advantageous. This thermal pretreatment takes place preferably in a conditioning receiver under a vacuum at temperatures of $200-800^\circ\text{C}$ for a period from 2 to 8 h.

The preparation of organometal compounds in accordance with formula I takes place, for example, by analogy with the methods described in US 3 932 307 and US 4 335 225. One possibility of producing them is the reaction of the transition metal halide with the corresponding Grignard reagent.

The preparation of the catalyst system in accordance with the invention takes place by mixing the individual components (a) to (d) in any way. However, it is preferred that the metallocenes (a) and aluminoxanes (b) first be mixed with each other, and then this mixture be mixed with the reaction product of metal oxides (c) and organometal compounds (d). It is further preferred that the individual components be mixed in an inert solvent such as a hydrocarbon, for example.

In another preferred method the preparation of the catalyst system in accordance with the invention takes place such that first the organometal compound of formula I is reacted with the thermally treated metal oxide. The two catalyst components are reacted in general in a ratio of about 0.01 to 1 mmol of organometal compound per gram of metal oxide. Preferred catalyst components are tetraneophylzirconium (TNZ) and hydroxylated Al_2O_3 . The preparation of this catalyst is described, for example, in US 4335225.

In a second step the metallocene and the aluminoxane are deposited on the catalyst that has been prepared in this way. For this the metallocene is first mixed with the aluminoxane. The mixing is preferably done in solution, with the metallocene being dissolved, for example, in an inert hydrocarbon and mixed with a solution of the aluminoxane. Examples of suitable inert solvents are aliphatic or aromatic hydrocarbons, with toluene being preferred. The concentration of the aluminoxane in the solution lies in the range of about 5 to 30% by weight, with respect to the total solution. The metallocenes are preferably used in an amount of 10^{-4} to 1 mol per mol of aluminoxane. The mixing time amounts to 5 min to 24 h, preferably 5 to 60 min. The operation is carried out at a temperature of -10 to $+70^\circ\text{C}$, in particular 10 to 40°C .

The deposition of the metallocene/aluminoxane reaction mixture on the catalyst support (metal oxide plus organometal compound of formula I) takes place preferably in a solution. For this the supported catalyst is coated with an inert solvent and then mixed with the solution of the metallocene/aluminoxane complex. Inert aliphatic and aromatic hydrocarbons are preferred as solvents. In particular, toluene is used. The reaction time is 10 min to 24 h, preferably 10 to 60 min. The process is carried out at a temperature of 0 to 80°C , in particular 10 to 50°C .

After the end of the reaction the solvent is driven off in a vacuum, after which the catalyst is washed several times with a low-boiling inert aliphatic substance. Preferably, n-pentane is used. The metallocene content of the catalyst system obtained in this way is preferably in the range between 0.01 to 1% by weight, especially preferably between 0.05 to 0.3% by weight, with respect to the weight of the overall catalyst.

The catalyst system in accordance with the invention is preferably used for polymerization of olefins such as ethylene, propene, butene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, cyclopentene, norbornene or norbornadiene.

Accordingly, another object of the invention is the use of the catalyst system in accordance with the invention for polymerization of olefins.

Another object of the invention is a method for producing polyolefins, in which the olefins are polymerized in the presence of the catalyst system in accordance with the invention. The production of polyolefin blends of isotactic and elastomeric polypropylenes, in which propylene, optionally together with other comonomers, is polymerized in the presence of the catalyst system in accordance with the invention is particularly advantageous.

The particular advantage of using the catalyst system in accordance with the invention lies in the fact that it is possible to produce polymer blends of isotactic and elastomeric stereoblock homo- and copolymers directly in the polymerization reaction in one step "in situ," where both the process step of mixing that was hitherto necessary for blends of this kind as well as the chemical degradation in order to achieve processable polymers with sufficiently low viscosity are omitted. The polymers produced in accordance with the invention are free flowing, have a compact spherical shape and can easily be processed.

Another advantage lies in the fact that it is possible to produce polymer blends with high molecular weights, both with broad and/or bimodal molecular weight distribution. For example, it is possible to produce high-molecular elastomeric PPs as well as low-molecular isotactic PPs directly in the reactor in one step.

The catalyst in accordance with the invention can be introduced into the polymerization mixture both as a powder as well as as a suspension in an inert hydrocarbon, for example, pentane, hexane, cyclohexane or mineral oils. The polymerization is carried out in the known way in a solution, suspension or gas phase method, continuously or batchwise, at a temperature of -10 to $+200^{\circ}\text{C}$, preferably $+20$ to $+80^{\circ}\text{C}$. Propene is polymerized, optionally together with other comonomers like ethylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, cyclopentene, norbornene or norbornadiene. Hydrogen is added as molecular weight regulator, if necessary. The overall pressure in the polymerization is 0.5-150 bar. Polymerization in the pressure range of 1 to 40 bar is preferred.

The amount of the support that is used is 0.1 to 1 g per liter of reaction volume, in particular, 0.2 to 0.6 g per liter of reaction volume. The amount of the transition metal compounds, with respect to the transition metal, is 10^{-3} to 10^{-8} mol of transition metal, preferably 10^{-4} to 10^{-7} mol per gram of support. The aluminoxane is used in a concentration of 10^{-6} to 10^{-1} mol, preferably 10^{-5} to 10^{-2} mol per gram of support.

If the polymerization is carried out as a suspension or solution polymerization, an inert solvent is used. For example, aliphatic or cycloaliphatic hydrocarbons like pentane, hexane or cyclohexane can be used. Toluene can also be used. Polymerization preferably is carried out in a liquid monomer. If inert solvents are used, propene is supplied in gas form or liquid form.

The length of the polymerization is 10 min to 6 h, preferably 1 to 3 h.

The following examples are intended to illustrate the invention in more detail.

Here:

M_w means the weight average molecular weight in g/mol } measured by GPC
 M_w/M_n molecular weight dispersion

MFI (230/2, 16) is the melt index measured in accordance with DIN 53735, 230°C melt temperature and 2.16 kg load

T_{m1} is the melt temperature 1 in °C } measured by DSC
 T_{m2} is the melt temperature 2 in °C }
 ΔH is the melting enthalpy in Joule/g }

A) Production of catalyst

1) Production of tetrancophylzirconium (TNZ)/Al₂O₃ supported catalyst

21.59 g purified TNZ (produced in accordance with DE-OS 43 21 496) is dissolved in 300 mL water-free hexane under a protected gas and transferred to a dropping funnel, then the solution prepared in this way is slowly added by drops to a solution of 171.25 g Al₂O₃ and 3.25 L hexane while stirring, and stirred for 14 h at room temperature. The aluminum oxide that is used is put into a heated and nitrogen-flushed conditioning receiver and heated red hot under a vacuum for 4 h at 385°C, then cooled under excess nitrogen pressure and kept at 1 bar until used. After the end of the reaction the excess solvent is driven off and then the mixture is dried to constant weight in a vacuum. The resulting supported catalyst has a TNZ content of 11.89% by weight. It can be kept under nitrogen as long as one wishes.

2) Immobilization of the metallocene/MAO complex on the TNZ/Al₂O₃ supported catalyst

7.5 mg ethylenebis(indenyl)zirconium dichloride (Witco) is dissolved in 10 mL toluene under nitrogen. Then 4.95 g of a 10.5% by weight MAO solution (methylaluminoxane, Witco) is slowly added by drops with stirring and then stirred for 15 min. The resulting catalyst solution is taken up with a syringe and, while stirring, added to 5.48 g of the TNZ/Al₂O₃ supported catalyst produced under 1). Then the mixture is stirred for another 45 min at room temperature, then the solvent is driven out under vacuum, the substance is washed two times with 20 mL pentane and dried. The catalyst prepared in this way has a metallocene content of 0.08% by weight. The Al(MAO):Zr(MC) mol ratio is 500:1.

B) Polymerization

Example 1

A 5-L double-jacket autoclave equipped with stirrer, thermostat jacket, rotary speed and rotary torque measurement that has been heated at 160°C and 0.1 mbar was filled with 500 g propene at 16°C after three propene/vacuum cycles. After increasing the stirrer speed to 400 rpm and heating the system to 30°C 2 g of the catalyst described under (A2) was washed in with 1000 g liquid propene. The reactor was heated to a working temperature of 60°C in the course of 10 min and then the stirrer speed was raised to 700 rpm. After a polymerization time of 2 h the stirrer speed was reduced to 150 rpm and the excess propylene was flash removed from the reactor while maintaining the working temperature, the reactor was again flushed with nitrogen, and then opened.

The remaining polymer was free flowing, nonadhesive and spherical. After stabilization and drying in a vacuum chamber at 50°C 71 g polymer was obtained (analysis data, see Table 1).

Example 2

Example 1 was repeated, but the catalyst had a metallocene content of 0.125% by weight, the Al(MAO):Zr(metallocene) mol ratio was 250:1. The reaction time was 2 h, the polymerization temperature was 60°C. The remaining polymer product was spherical, free flowing and not adhesive. 78 g was obtained (see Table 1).

Example 3

The polymerization took place by analogy with Example 1, but the catalyst had a metallocene content of 0.125% by weight, the Al(MAO):Zr(metallocene) ratio was 125:1. The polymerization temperature was 60°C, the polymerization time was 2 h.

An elastic polymer product with fine grained, free flowing structure was obtained. After processing in accordance with Example 1, a yield of 107 g was achieved.

Example 4

2.08 g of the catalyst produced under (A2) was used for polymerization of propene by analogy with Example 1. However, the catalyst had a metallocene content of 0.288% by weight. The Al(MAO):Zr(metallocene) ratio was 125:1. The polymerization temperature was 60°C, the polymerization time was 2 h. The resulting polymer was free flowing, nonadhesive and had a broad particle size distribution. The yield of the processed product was 201 g (see analysis results, Table 1).

Example 5

2.12 g of the catalyst produced under (A2) (metallocene content 0.283% by weight) was used for polymerization of propene in accordance with Example 1. The Al(MAO):Zr(metallocene) ratio was 125:1. In contrast to Example 1, 1300 g propene was present in the reactor, the catalyst was introduced at the polymerization temperature of 60°C with 200 g propene and a nitrogen pressure of 40 bar. The reaction time was 2 h. After the end of the polymerization a free flowing granular product was obtained. The yield was 51 g.

Example 6

The polymerization took place by analogy with Example 5. The amount of catalyst was 2 g, with a metallocene content of 0.1% by weight. The Al(MAO):Zr(metallocene) ratio was 250:1. A yield of 105.4 g was obtained. The product was free flowing and granular in structure.

Example 7

Example 6 was repeated, the metallocene content was 0.2% by weight. After 2 h the polymerization was stopped. 381.2 g of a free flowing, spherical, nonadhesive product was obtained.

Example 8

The polymerization of Example 6 was repeated, but the metallocene content of the catalyst was 0.3% by weight. A yield of 652.3 g was obtained. The product was free flowing and fine grained.

Comparison Example 1

2.03 g of a pure TNZ/Al₂O₃ supported catalyst was reacted with MAO by analogy with Example (A2). The addition of a metallocene was eliminated. The MAO:Zr(TNZ) mol ratio was 5:1. Polymerization took place by analogy with Example 1, with 17 g of a polymer product that was not free flowing and tended to be adhesive was obtained. The polymer is unsuitable for further processing.

Table 1

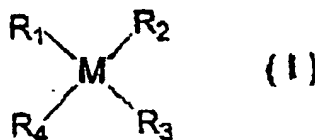
Beispiel ^①	Aktivität ^② (kg PP/mol Zr ⁴⁺)	M _w (g/mol)	M _w /M _n	MEI (g/10min)	T _{m1} (°C)	T _{m2} (°C)	ΔH ₁ (J/g)	ΔH ₂ (J/g)
1	83,7	978000	32	0,67	134	148	40	13
2	93,6	828000	25	1,23	133	146	41	13
3	126,1	2200000	6	<0,01	131	151	-	-
4	236,5	920000	27	172	132	151	-	-
5	251,2	854000	26	228	133	153	-	-
6	128,1	-	-	698	134	151	-	-
7	468	925000	16	<0,01	132	152	-	-
8	807,9	1990000	10	<0,01	131	152	-	-
Vergleichsbeispiel ^③	53,7	n.b.*	n.b.*	n.b.*	-	148	-	-

^④ n. b. nicht bestimmbar (Ausschlußgrenze GPC)

Key:	1	Example
	2	Activity (kg PP/mol Zr ⁴⁺ h)
	3	Comparison Example I
	4	*n.b. = not determinable (GPC exclusion limit)

Claims

1. A catalyst system for olefin polymerization, containing
 - a) Metallocenes of transition metals of the III, IV, V and VI subgroups of the periodic system, where the inner transition elements of the lanthanides also fall under subgroup III,
 - b) Aluminoxanes,
 - c) Metal oxides of main groups II, III and IV of the periodic system,
 - d) Organometal compounds of formula I



where

M is a transition metal of the subgroups III, IV, V or VI of the periodic system, including the lanthanides and

R₁ to R₄ can be the same or different and mean an allyl, benzyl, neophyl or neopentyl residue.

2. A catalyst system as in Claim 1, which is characterized by the fact that metallocenes based on substituted or unsubstituted, symmetric or asymmetric cyclopentadienyl, indenyl or fluorenyl metallocenes are used.

3. A catalyst system as in Claim 1 or 2, which is characterized by the fact that metallocenes based on Ti, Zr, Hf are used.

4. A method for producing a catalyst system as in one of Claims 1 to 3, which is characterized by the fact that first the metallocenes (a) and aluminoxanes (b) are mixed with each other, and this mixture is then mixed with the reaction product of metal oxides (c) and organometal compounds (d).

5. The use of the catalyst system as in one of Claims 1 to 3 for polymerization of olefins.

6. A method for producing olefins, which is characterized by the fact that olefins are polymerized in the presence of the catalyst system in accordance with one of Claims 1 to 3.

7. A method for producing polyolefin blends of isotactic and elastomeric polypropylenes, which is characterized by the fact that propylene, optionally together with other comonomers, is polymerized in the presence of the catalyst system in accordance with one of Claims 1 to 3.

European
Patent Office

Application Number
EP 95 11 1478

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT													
Category	Citation of document with indication where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ⁶)										
X	WO-A-87 02991 (EXXON CHEMICAL PATENTS INC) * Claims 1, 7, 9, 12 * * Page 7, line 16 - line 33 *	1-3,5,6	C08F19/00										
A	EP-A-0 546 690 (NIPPON OIL CO LTD) * Page 24; Example IE29; Table 3 *	1											
A	US-A-4 411 821 (EDWARD G. HOWARD) * Claim 1 * * Examples 1, 2 *	1											
The present search report has been drawn up for all claims.			TECHNICAL FIELDS SEARCHED (Int. Cl. ⁶) C08F										
Place of search THE HAGUE		Date of completion of the search October 27, 1995	Examiner Fischer, B										
<p align="center">CATEGORY OF CITED DOCUMENTS</p> <table border="0"> <tr> <td>X: Particularly relevant if taken alone.</td> <td>T: Theory or principle underlying the invention.</td> </tr> <tr> <td>Y: Particularly relevant if combined with another document of the same category.</td> <td>E: Earlier patent document, but published on, or after the filing date.</td> </tr> <tr> <td>A: Technological background.</td> <td>D: Document cited in the application.</td> </tr> <tr> <td>O: Non-written disclosure.</td> <td>L: Document cited for other reasons.</td> </tr> <tr> <td>P: Intermediate document.</td> <td>&: Member of the same patent family, corresponding document.</td> </tr> </table>				X: Particularly relevant if taken alone.	T: Theory or principle underlying the invention.	Y: Particularly relevant if combined with another document of the same category.	E: Earlier patent document, but published on, or after the filing date.	A: Technological background.	D: Document cited in the application.	O: Non-written disclosure.	L: Document cited for other reasons.	P: Intermediate document.	&: Member of the same patent family, corresponding document.
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Translated from German

- 19- European Patent Office
- 11- EP 0 695 765 A1
- 12- EUROPEAN PATENT APPLICATION
- 43- Publication Date: February 07, 1996, Patent Bulletin 1996/06
- 21- Application Number: 95111478.4
- 22- Application Date: July 21, 1995
- 51- International Classification⁶: C08F 10/00
-
- 84- Contractual Countries Named:
AT BE DE ES FR GB IT NL
- 30- Priority: August 01, 1994 AT 1512/94
- 71- Applicant: PCD-Polymere Gesellschaft m. b. H.
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-
- 54- A catalyst system and a process for the polymerization of olefins
- 57- A catalyst system on the basis of metallocenes, aluminoxanes, organic transition metal compounds, and a catalyst carrier support. The new catalysts may be used advantageously for the polymerization of olefins.

EP 0 695 765 A1

Description

The invention is about a heterogeneous catalyst system for the polymerization of olefins, and a polymerization process for the production of polyolefins, especially of polypropylenes (PP) and its copolymers which are obtained directly in the reactor as blends of isotactic polypropylenes and stereoblock polypropylenes respectively its copolymers.

The preparation of stereoblock polypropylenes respectively elastomer polypropylenes (ELPP) which essentially have a stereoregular block arrangement in the chain structure, with alternating isotactic and atactic PP sequences in the polymer chain, is possible by the polymerization of propylene, possibly together with other comonomers, using special catalysts. Such catalysts may be, for example, organometallic Ti-, Zr- or Hf compounds on an oxide carrier support (US 4335225), metallocene catalysts in combination with aluminoxanes (US 4522982) or reaction products of magnesium alkoxides with a tetravalent titanium chloride in the presence of special electron donors (US 5118 768).

In the processing of the elastomer polypropylenes prepared with these catalysts it shows, though, that the products agglomerate very easily and do not flow freely. Further processing is made more difficult by the formation of lumps and sticking and adhering to transporting- and apparatus parts.

The German Disclosure Document DE-OS 43 21 496 does away with that disadvantage by using a special Zr carrier catalyst in liquid propene and mixing after the polymerization with a polar solvent or with CO₂ to precipitate the generated polypropylene.

It is furthermore known that it is possible to prepare isotactic polypropylene (IPP) with metallocenes in combination with methyl aluminoxanes (Hoe EP-A-485823). These isotactic polypropylenes stand out by their narrow molar mass distribution and their high crystallinity. The disadvantage is that the products are in powder form and thus unsuitable for technical application purposes.

Also known is that mixed catalysts, consisting of a metallocene and a conventional Ziegler-Natta catalyst are used for the production of isotactic polyolefins, especially of isotactic polypropylene. For this it is required to fixate the metallocene onto the heterogeneous Ziegler-Natta system. The polymers have a high isotactic portion and a broad molar mass distribution (Fina EP-A-0536104). The products, however, are of a high stiffness, and that is a disadvantage for special applications.

The disadvantages described can be removed by mixing high-molecular, elastomer PP and conventional isotactic PP, and it is possible to produce tailor-made polymer blends, optimally suited for the respective purpose of use. DE-OS 43 30 341 describes ELPP/IPP blends as kneaded mixtures. These blends stand out by their increased raw strength at decreased stiffness, which is an advantage for many applications, such as for example, the production of films, hoses, concertina walls etc. To be able to technically process these high-molecular mixtures it is necessary to first chemically degrade both components in an extruder, as another processing step in addition to the mixing process.

The task was therefore to develop a catalyst system and a polymerization process in which the disadvantages described above are avoided and which in particular make it possible in a simple process and directly in the reactor, to produce flowable polypropylene reactor blends in an "in-situ" reaction. The task was solved by using a catalyst system on the basis of a metallocene, an aluminoxane, an organic transition metal compound, and a catalyst carrier support.

The subject of the invention is thus a catalyst system for the polymerization of olefins, containing

- metallocenes from transition metals of the IIIrd, IVth, Vth and VIth subgroup of the periodic system where the inner transition elements of the lanthanoids are also part of the IIIrd subgroup,
- aluminoxanes,
- metal oxides of the IIrd, IIIrd and IVth main group of the periodic system,
- organometallic compounds of formula I



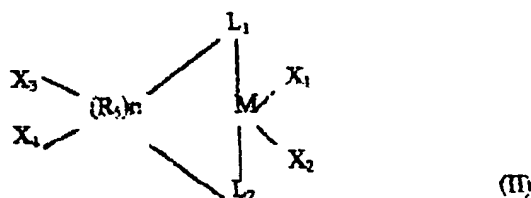
>> page 3

in which

M denotes a transition metal of the IIIrd, IVth, Vth or VIth subgroup of the periodic system, including the lanthanoids,

R₁ to R₄ may be identical or different and denote an allyl-, benzyl-, neophyl- or neopentyl rest.

As to metallocenes, all compounds may be used that are made from a transition metal as the central atom and coordination ligands on the basis of substituted or unsubstituted uni- or multinuclear hydrocarbons - which may form a sandwich structure with the central atom - or on the basis of amido-, phosphido- or arsenido rests; the coordination ligands may also be connected via binding links. Such metallocenes are described, for example, in DE-OS 44 17 542 (PCD), EP-A 336 128 (Hoechst) or EP-A-536 104 (Fina). Preferably used are metallocenes on the basis of substituted or unsubstituted, symmetrical or asymmetrical cyclopentadienyl-, indenyl- or fluorenyl metallocenes of formula II,



where

M denotes a transition metal as in formula I,

X₁ to X₄ are identical or different and denote a C₁ - C₁₀ alkyl group, a C₁ - C₁₀ alkoxy group, a C₆ - C₁₀ aryl group, a C₆ - C₁₀ aryloxy group, a C₂ - C₁₀ alkenyl group, a C₇ - C₂₀ arylalkyl group, a C₇ - C₂₀ alkylaryl group, a C₈ - C₂₀ arylalkenyl group, hydrogen or a halogen atom,

L₁ and L₂ are identical or different and denote a substituted or unsubstituted cyclopentadienyl-, indenyl- or fluorenyl rest,

R₅ may be carbon, silicon, germanium or tin,

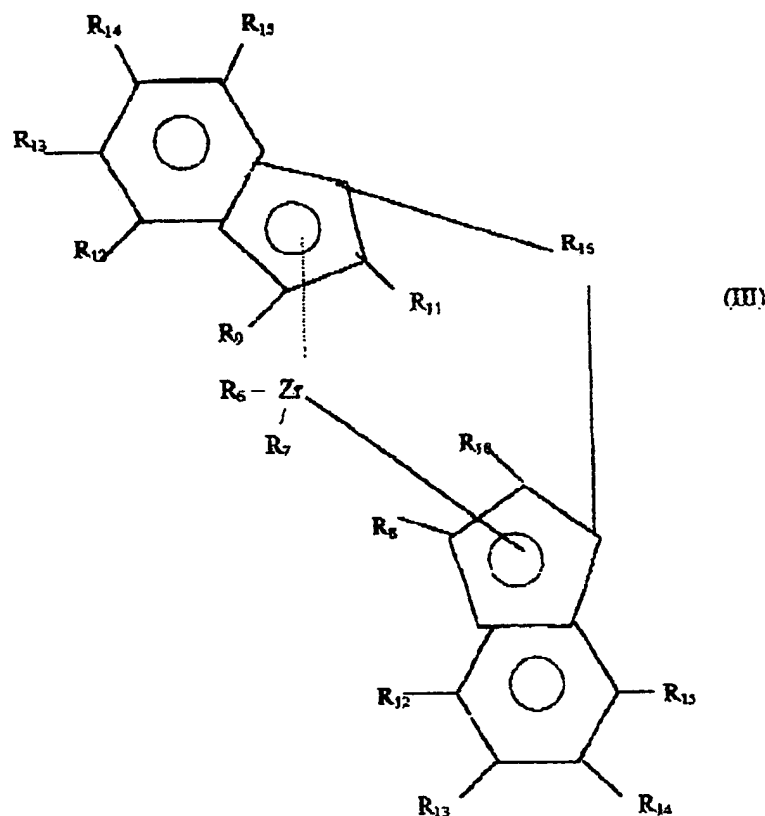
n stands for an integer from 0 to 4, and in case n = 0, the free valences at L₁ and L₂ are substituted by a rest X₁ to X₄,

as is known, for example, from DE-OS 44 17 542.

Furthermore preferred are catalyst systems in which the central atom of the metallocenes is Ti, Zr or Hf.

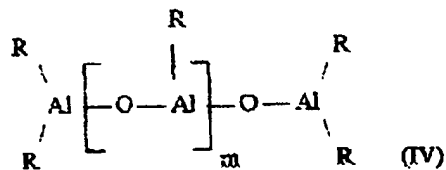
>> page 4

Formula III shows, as an example, another metallocene preferably used in accordance with the invention, with a Zr central atom on the basis of an indenyl coordination ligand:

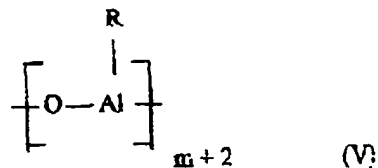


where
 R_6 and R_7 are identical or different and are a halogen atom, a $C_1 - C_{10}$ alkyl group or a $C_1 - C_{10}$ alkoxy group,
 R_8 to R_{11} are identical or different and are a halogen atom, a $C_1 - C_{10}$ alkyl group or a $C_6 - C_{10}$ aryl group,
 R_{12} to R_{15} are identical or different and are a halogen atom, a $C_1 - C_{10}$ alkyl group, a $C_6 - C_{10}$ aryl group, a $C_2 - C_{10}$ alkenyl group, and
 R_{16} is a $-CH_2-CH_2-$, a $Si(CH_3)_2$ or a $C(CH_3)_2$ bridge.

As to aluminoxanes, it is possible to use linear



as well as cyclic aluminoxanes



where in the formulae IV and V, the rests may be identical or different and denote a $C_1 - C_{10}$ alkyl group, a $C_6 - C_{10}$ aryl- resp. alkylaryl group, and m an integer from 1 - 50. Preferably the rests are identical and stand for methyl, isobutyl, phenyl or benzyl; methyl is particularly preferred. The aluminoxane can be

prepared in various ways in accordance with known methods. One possibility is, for example, the reaction of aluminum alkyls with aluminum sulfate containing crystal water (Hoechst EP-A-302424). It is particularly advantageous to use customary commercial MAO (Methylaluminoxane, Witco Co., Germany).

The inorganic oxides of the metals of the IInd to the IVth main group of the periodic system are customary carrier support materials for catalysts. Preferred are the oxides of the metals magnesium, calcium, aluminum, silicon, boron, and mixtures thereof. Particularly preferred are, for example, the commercially available aluminum oxides "Alumina Typ C" (Degussa Co.) and silicon oxides of the type "Silica Davison Grade 952 - 957", and mixtures of Al_2O_3 and SiO_2 .

A thermal pretreatment of the inorganic carrier in an inert gas flow or in a vacuum at temperatures of 30 - 1000 °C over 1 - 50 hours is advantageous. This thermal pretreatment preferably takes place in a conditioning vessel under a vacuum at temperatures of 200 - 800 °C over a time of 2 - 8 hours.

The preparation of the organometallic compounds in accordance with formula I takes place, for example, analogously to the processes described in US 3 392 307 and US 4 335 225. One possibility of preparation is the reaction of the transition metal halide with the corresponding Grignard reagent.

The preparation of the catalyst system in accordance with the invention takes place by mixing the individual components a) to d) in any order. It is preferred, though, to first mix the metallocenes (a) and aluminoxanes (b) with each other, and then mixing this mixture with the reaction product from metal oxides (c) and organometal compounds (d). It is furthermore preferred to mix the individual components in an inert solvent, such as for example a hydrocarbon.

In another preferred version, the preparation of the catalyst system in accordance with the invention takes place by first reacting the organometallic compound of formula I with the thermally pretreated metal oxide. Generally, the two catalyst components are reacted in a ratio of about 0.01 to 1 mmol of the organometallic compound per gram of metal oxide. Preferred catalyst components are tetraneophyl zirconium (TNZ) and hydroxylated Al_2O_3 . The preparation of this catalyst is described, for example, in US 4335225.

In a second step, the metallocene and the aluminoxane are applied onto the carrier thus prepared. For this, the metallocene is first mixed with the aluminoxane. The mixing preferably takes place in solution, where the metallocene is dissolved, for instance, in an inert hydrocarbon, and mixed with a solution of the aluminoxane. Suitable as inert solvents are, for example, aliphatic or aromatic hydrocarbons; toluene is preferred. The concentration of the aluminoxane in the solution is in the range of about 5 to 20 % by weight, relative to the total solution. The metallocenes are preferably used in an amount of 10^{-4} to 1 mole per mole aluminoxane. The mixing time is 5 min to 24 hours, preferably 5 to 60 minutes. The work is done at a temperature of -10 to +70 °C, especially at 10 to 40 °C.

Applying the metallocene/aluminoxane reaction mixture onto the carrier catalyst (metal oxide plus organometallic compound of formula I) is preferably done in solution. For this, an inert substance is added to the carrier catalyst to form a lower layer, and then it is stirred with the solution of the metallocene/aluminoxane complex. Inert aliphatic and aromatic hydrocarbons are preferred as solvents, especially toluene is used. The reaction time is 10 min to 24 hours, preferably 10 to 60 minutes. The work is done at a temperature of 0 to 80 °C, especially at 10 to 50 °C.

After the reaction is finished, the solvent is drawn off in a vacuum, then washed several times with an inert aliphatic of a low boiling point. Preferably, n-pentane is used. The metallocene content of the catalyst system thus obtained is preferably in the range between 0.01 to 1 % by weight, particularly preferred between 0.05 and 0.3 % by weight, relative to the mass of the total catalyst.

The catalyst system in accordance with the invention is preferably used for the polymerization of olefins, such as e.g. ethylene, propylene, butene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, cyclopentene, norbornene or norbornadiene. Accordingly, another subject of the invention is the use of the catalyst system in accordance with the invention for the polymerization of olefins.

Another subject of the invention is a process for the production of polyolefins, in which the olefins are polymerized in the presence of the catalyst system in accordance with the invention. Particularly advantageous is the preparation of polyolefin blends of isotactic and elastomer polypropylenes in which propylene, possibly together with additional comonomers, is polymerized in the presence of the catalyst system in accordance with the invention.

The particular advantage of using the catalyst system in accordance with the invention is that it becomes possible to prepare polymer blends of isotactic and elastomer stereoblock homo- and copolymers directly in the polymerization reactor, in one step "in situ"; the processing step of mixing, hitherto necessary for such blends, as well as the chemical degradation to obtain processible polymers of a sufficiently low viscosity, are therefore not necessary anymore. The polymers produced in accordance with the invention are quite flowable, have a compact spherical shape, and can be processed well.

Another advantage is the possibility of producing polymer blends of high molar masses, and with a broad and/or bimodal molecular mass distribution. It is thus possible, for example, to produce in one step high-molecular elastomer PP as well as low-molecular isotactic PP directly in the reactor.

>> page 6

The catalyst in accordance with the invention can be inserted into the polymerization mixture as a powder, but also as a suspension in an inert hydrocarbon, for example pentane, hexane, cyclohexane or mineral oils. The polymerization is carried out in a known way in a solution-, suspension- or gaseous phase process, continuously or discontinuously, at a temperature of -10 to $+200$ °C, preferably $+20$ to $+80$ °C. The polymerization is done with propene, possibly together with additional comonomers such as e.g. ethylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, cyclopentene, norbornene or norbornadiene. If necessary, hydrogen is added as a molar mass controller. The total pressure in the polymerization is 0.5 to 150 bar. The polymerization is preferably in the pressure range of 1 to 40 bar.

The amount of carrier support used is 0.1 to 1 g per liter of reactor volume, especially 0.2 to 0.6 g per liter of reactor volume. The amount of the transition metal compounds, relative to the transition metal, is 10^{-3} to 10^{-5} mole transition metal, preferably 10^{-4} to 10^{-7} mole, per gram of carrier. The aluminoxane is used in a concentration of 10^{-6} to 10^{-3} mole, preferably 10^{-5} to 10^{-2} mole, per gram of carrier.

If the polymerization is carried out as a suspension- or solution polymerization, an inert solvent is used. For example, aliphatic or cycloaliphatic hydrocarbons may be used, such as pentane, hexane or cyclohexane. Toluene is suitable too. Polymerization is preferably done in liquid monomer. If inert solvents are used, propene is dosed in in gaseous or liquid form.

The duration of the polymerization is 10 min to 6 hours, preferably one to three hours.

The examples that follow may further elucidate the invention.

The abbreviations mean the following:

M_w molar mass (weight average), in g/mole } determined by gas chromatography
 M_w/M_n molar mass dispersity

MFI (230/2.16) melting index, measured in accordance with DIN 53735; 230 °C melting temperature and 2.16 kg load.

T_{m1}	melting temperature 1, in °C	} determined by DSC
T_{m2}	melting temperature 2, in °C	
ΔH	enthalpy of fusion, in Joule/g	

A) Preparation of the catalyst

1) Preparation of the tetranecophyl zirconium (TNZ) / Al_2O_3 carrier catalyst

21.59 g of purified TNZ (preparation in accordance with DE-OS 43 21 496) are dissolved under protective gas in 300 ml of dry hexane and transferred to a dropping funnel; then the solution thus prepared is slowly added in drops, while stirring, to a suspension of 171.25 g of Al_2O_3 and 3.25 l of hexane, and stirred at room temperature for 14 h. The aluminum oxide used is filled into a conditioning vessel that had been thoroughly heated out and rinsed with nitrogen. It is annealed for 4 h under a vacuum at 385 °C and degassed, then cooled under an excess pressure of nitrogen and stored at 1 bar until used. After the reaction has ended, the excess solvent is drawn off and then dried in a vacuum to constancy of weight. The carrier catalyst thus obtained has a TNZ content of 11.89 % by mass. It can be stored indefinitely under nitrogen.

2) Fixing the metallocene/MAO complex onto the TNZ/ Al_2O_3 carrier catalyst

7.5 mg of ethylenebis(indenyl) zirconium dichloride (Witco Co.) is dissolved under nitrogen in 10 ml of toluene. Then 4.95 g of a MAO solution of 10.5 % by mass (methylaluminoxane, Witco Co.) is slowly added in drops and stirred for 15 min. The catalyst solution thus obtained is taken up with a syringe and added to 5.48 g of the TNZ/ Al_2O_3 carrier catalyst prepared under 1), while stirring. It is then stirred at room temperature for another 45 min, then the solvent is drawn off under a vacuum, washed twice with 20 ml of pentane and dried. The catalyst thus prepared has a metallocene content of 0.08 % by mass. The molar ratio $Al(MAO) : Zr(MC)$ is 500 : 1.

>> page 7

B) Polymerization

Example 1

A 5 liter double-jacket autoclave with stirrer, thermostat jacket, and measuring instruments for temperature, stirring speed and torque, heated out at 160 °C and 0.1 mbar, is filled with 500 g of propane after three propane/vacuum cycles. After increasing the stirring speed to 400 rpm and heating the system to 30 °C, 2 g of the catalyst described under A2) are flushed in with 1000 g of liquid propene. The reactor was heated over 10 min to a working temperature of 60 °C, and the stirring speed was increased to 700 rpm. After a polymerization time of 2 h, the stirring speed was decreased to 150 rpm, the excess propylene was flashed off while keeping the working temperature, it was rinsed with nitrogen once again, and then the reactor was opened.

The remaining polymer was flowable, not adhesive and spherically shaped. After stabilizing and drying in a vacuum cabinet at 50 °C, 71 g of polymer were obtained (analysis data see Table 1).

Example 2

Example 1 was repeated, but the catalyst had a metallocene portion of 0.125 % by mass, the molar ratio of $Al(MAO) : Zr(\text{metallocene})$ was 250 : 1. The reaction time was 2 h, the polymerization temperature 60 °C. The remaining polymer product was spherically shaped, flowable and non-adhesive. The yield was 78 g (compare Table 1).

Example 3

The polymerization took place analogously to example 1, but the catalyst had a metallocene content of 0.125 % by mass, the ratio of $Al(MAO) : Zr(\text{metallocene})$ was 125 : 1. The polymerization temperature was 60 °C, the duration of the polymerization was 2 h.

Obtained was an elastic polymer product of a fine, flowable structure. After processing in accordance with example 1, a yield of 107 g was obtained.

Example 4:

2.08 g of the catalyst prepared under A2) were used for the polymerization of propene analogously to example 1. The catalyst, however, had a metallocene content of 0.288 % by mass. The ratio of Al(MAO) : Zr(metallocene) was 125 : 1. The polymerization temperature was 60 °C, the duration of the polymerization was 2 h. The polymer obtained was flowable, non-adhesive, and had a broad distribution of grain size. The yield of the processed product was 201 g (compare analysis results, Table 1).

Example 5:

2.12 g of the catalyst prepared under A2) (metallocene content 0.283 % by mass) were used in accordance with example 1 for the polymerization of propene. The Al(MAO) : Zr(metallocene) ratio was 125 : 1. Different from example 1, 1300 g of propene were inserted initially, the catalyst was flushed in at the polymerization temperature of 60 °C with 200 g of propene and a nitrogen pressure of 40 bar. The reaction time was 2 h. After the polymerization was ended, a flowable, granular product was obtained. The yield was 51 g.

Example 6

The polymerization took place analogously to example 5. The amount of catalyst was 2 g, with a metallocene content of 0.1 % by mass. The Al(MAO) : Zr(metallocene) ratio was 250 : 1. A yield of 105.4 g was obtained. The product was flowable, of a granular structure.

Example 7:

Example 6 was repeated, the metallocene content was 0.2 % by mass. After 2 hours, the polymerization was terminated. 381.2 g of a flowable, spherical, non-adhesive product were obtained.

Example 8:

The polymerization of example 6 was repeated, but the metallocene content of the catalyst was 0.3 % by mass. A yield of 652.3 g could be obtained. The product was flowable and finely granulated.

>> page 8

Reference example I:

2.03 g of a pure TNZ/Al₂O₃ carrier catalyst were reacted with MAO analogously to example A2). The addition of metallocene was done without. The molar ratio MAO : Zr(TNZ) was 5 : 1. The polymerization took place analogously to example 1, and 17 g of a polymer product were obtained; it was not flowable and tended to be adhesive. The polymer

>> page 9

is unsuitable for further processing.

Table I:

Example	Activity (kg PP/mole Zr ⁴⁺ h)	M _w (g/mole)	M _w /M _n	MFI (g/10 min)	T _m (°C)	T _{cd} (°C)	ΔH ₁ (J/g)	ΔH ₂ (J/g)
1	83.7	979000	32	0.67	134	148	40	13
2	93.6	828000	25	1.23	133	148	41	13
3	126.1	2200000	6	< 0.01	131	151	-	-
4	236.5	920000	27	172	132	151	-	-
5	251.2	854000	26	226	133	153	-	-
6	128.1	-	-	699	134	151	-	-
7	468	925000	15	< 0.01	132	152	-	-
8	807.9	1990000	10	< 0.01	131	152	-	-
Reference example	53.7	n.d.*	n.d.*	n.d.*	-	148	-	-

*n.d. not determinable (exclusion limit GPC)

Patent claims

1. A catalyst system for the polymerization of olefins, containing

- a) metallocenes from transition metals of the IIIrd, IVth, Vth and VIth subgroup of the periodic
- b) aluminoxanes,
- c) metal oxides of the IIrd, IIIrd and IVth main group of the periodic system,
- d) organometallic compounds of formula I



in which

M denotes a transition metal of the IIIrd, IVth, Vth or VIth subgroup of the periodic system,
and
R₁ to R₄ may be identical or different and denote an allyl-, benzyl-, neophyl- or neopentyl rest.

- 2. A catalyst system in accordance with claim 1, characterized by the fact that metallocenes on the basis of substituted or unsubstituted, symmetrical or asymmetrical cyclopentadienyl-, indenyl- or fluorenyl metallocenes are present.
- 3. A catalyst system in accordance with claim 1 or 2, characterized by the fact that metallocenes on the basis of Ti, Zr, Hf are present.
- 4. A process for the production of a catalyst system in accordance with one of the claims 1 to 3, characterized by the fact that first, the metallocenes (a) and aluminoxanes (b) are mixed with each other, and that this mixture is then mixed with the reaction product of the metal oxides (c) and the organometal compounds (d).
- 5. The use of the catalyst system in accordance with one of the claims 1 to 3, for the polymerization of olefins.
- 6. A process for the production of polyolefins, characterized by the fact that olefins are polymerized in the presence of the catalyst system in accordance with one of claims 1 to 3.
- 7. A process for the production of polyolefin blends of isotactic and elastomer polypropylenes, characterized by the fact that propylene – possibly together with additional comonomers – is polymerized in the presence of the catalyst system in accordance with one of claims 1 to 3.

RELEVANT DOCUMENTS

Category	Identification of documents with indication of relevant parts, where applicable	Concerns Claim #	Classification of Application (Int. Cl. 6)
X	WO-A-87 02991 (EXXON CHEMICAL PATENTS INC) * Claims 1, 7, 9, 12 * * Page 7, line 16 - line 33 *	1-3, 5, 6	C08F10/00
A	EP-A-0 546 690 (NIPPON OIL CO LTD) * Page 24; example UE29; Table 3 *	1	
A	US-A-4 411 821 (EDWARD G. HOWARD) * Claim 1 * * Examples 1, 2 *	1	

AREAS RESEARCHED
(Int. Cl. 6)

C08F

This research report was drawn up for all patent claims.

Place of Research THE HAGUE	Final Date of Research October 27, 1995	Examined by Fischer, B
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CATEGORY OF DOCUMENTS NAMED:

X: considered of special importance by itself	T: theories or principles on which the invention is based
Y: considered of special importance in combination with another publication of the same category.	E: older patent document published on or after the day of application
A: technological background	D: document cited in the application
O: non-written disclosure	L: document cited for other reasons
P: related literature	&: member of the same family of patents, document corresponds

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